Review of experimental investigation on directly irradiated particles solar reactors

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ABSTRACT

Solar thermochemistry is a technology that has been demonstrated to contain a high potential development capability. In order to carry out efficient solar chemical reactions, optimized reactors adapted to each chemical process are necessary. In last 30 years many solar reactors of different configurations, performances and sizes have been designed and fabricated by the main solar chemistry research groups. Among them, directly irradiated particles solar reactors operate in a high temperature range that usually correspond to gas–solid thermochemical reactions. This work compiles more than 20 directly irradiated particles reactors designed, constructed and experimentally investigated in the last 30 years. Their description, schemes and main parameters of their performance are given. Detected problems associated are also mentioned. Reactors are classified from the point of view of chemical engineering in entrained, fluidized and stacked beds. Finally, a summary of the main characteristics of reviewed reactors is provided.

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Contents

1. Introduction

The objective of solar chemistry is to use solar radiation for producing fuels and chemicals [1]. It transforms solar energy in long-term storable and transportable energy carriers, what represents a significant contribution to the requirements for improving the current energetic system. In order to increase the efficiency, these processes should be performed at an upper temperature as high as possible because the rate of chemical reaction increases

exponentially with temperature. To achieve that, apart from an adequate concentration system, optimized solar reactors capable to withstand high temperatures, minimizing heat loss and favouring mass and heat transfer between chemicals involved are required. Solar reactors are particular cases of solar receivers where the absorber heat is employed to carry out endothermic chemical reactions. Thus, a preliminary classification of solar reactor could correspond to that generally used to categorize solar receivers. According to the heat integration mode into the reaction chamber, solar reactors are indirectly or directly irradiated [2].

1.1. Indirect reactors

The external opaque walls of the reaction chamber are heated by solar energy. Endothermic reactions are promoted by the heat flux transferred by conduction from the walls to the reactants. Most of indirect irradiated reactors found in literature are catalytic tubular reformers [3–7] where the catalyst is fixed inside a tube and the gas is forced to flow across. The solar flux is distributed along the external walls of the tubes. Additional concepts of indirect reactors have been also developed for thermochemical applications, such as double-cavity reactors with a reaction chamber physically separated from the one that receives the radiation [8–10].

1.2. Direct reactors

Reactants are directly irradiated and heated by incoming solar concentrated radiation. Reactors are opened to air or closed by a transparent window through which radiations enters into the reaction chamber. Due to the absorption of radiation occurs on the reactants surface, higher temperatures are expected by working with directly irradiated reactors. Apart from volumetric reactors, which physical processes have been widely studied from the point of view of volumetric absorbers [11,12], particles solar reactors represents the largest group of studied solar reactors, particularly in a laboratory scale. Thus, a compilation and examination of designed, constructed and experimentally investigated hitherto particles solar reactors are the aims of the present work.

2. Early studies on particles absorbance

Sandia National Laboratories (SNL) was pioneer in proposing solid particles as heat absorber medium for concentrated solar systems. The initial study was made by Martin and Vitko [13]. Pebbles and sand were tested as heat solid carriers with successful results. Detected advantages of such as scheme included direct absorption of the incident radiation, direct heat transfer, use of the working fluid as a storage medium, and ease of hybridizing with a fossil-fired system. Moreover, higher temperatures were theoretically possible. Their study led to the first concept of Solid Particle Central Receiver (SPCR) consisting in a falling cloud of 100–1000 μm solid particles [14]. Solar energy was directed to the particles through the aperture of a cavity receiver [14,15]. By means of a theoretical parametric study they analyzed how the material kind, the particles size or the infrared scattering albedo affected to the particles temperature, the convective loss and the optical thickness. Further studies were done on this topic, most of them collected on internal reports of SNL [16–20]. Such as research line concluded to a prototype of SPR that was tested on top of Sandia's 61 m tall central receiver located at the National Solar Thermal Test Facility in Albuquerque, NM. The heliostat field of this facility is able to provide 5 MW$_{th}$ [21].The SPR consisted of a 6 m tall cavity through where a 1 m wide curtain of spherical ceramic particles was dropped and directly heated with
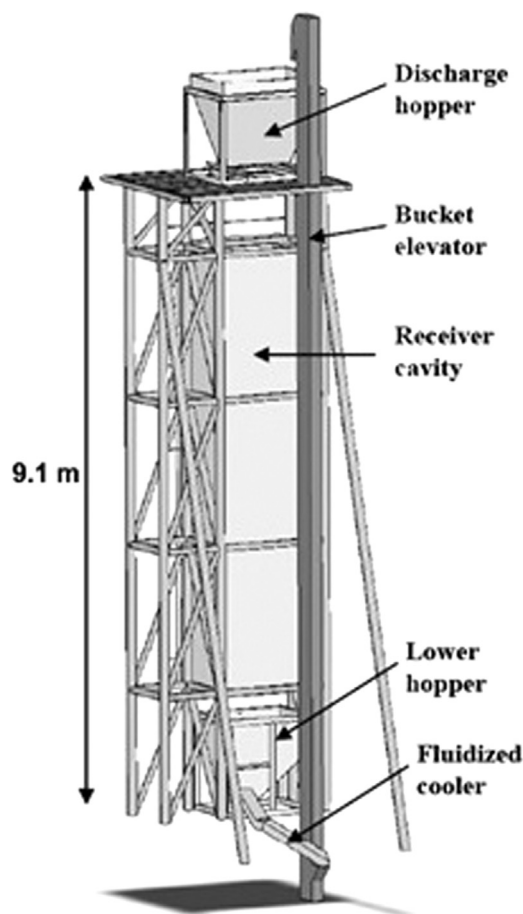

Fig. 1. Lay out of the SPCR developed in SNL [21].

concentrated solar energy. Particles were collected in an internally insulated lower hopper. Fig. 1 shows the system layout. First experimental research demonstrated a cavity temperature higher than 1000 °C, receiver efficiency in excess of 55% and particle exit temperature in excess of 200 °C, depending on the operating conditions. Siegel and Kolb [21] reported an expected improvement of the results after an optimization of the receiver design.

In fact, SNL are still in the process of developing SPCR. In 2012 DOE's SunShot Initiative awarded three research projects in this area that currently have been developed by SNL, NREL and San Diego State University.

Some other studies on particles receivers have been found in literature. For example, Bertocchi et al. [22] reported experimental evaluation of a solar particle receiver designed for a power input of 10 kW. It consisted of a conical cavity of 40 mm high and 78 mm of inner diameter close to the ambient by a quartz window. Particles were injected in a gas/particle suspension at the focal plane through a duct placed close to the window. The exit takes place at the rear of the receiver. Achieved exit gas temperatures exceeded 2100 K.

3. Particles reactors classification

The knowledge developed on particles receivers helped to the conception of the first receiver-reactors where particles perform both heat absorption and chemical transformation. Particles may be arranged with different configuration depending on their required residence time inside the reactor and the existence of a

carrier fluid and its contact mode with the particles. These parameters affect directly to the heat and mass transfer occurring inside the reaction zone. Thus, particles solar reactors can be distinguished, according to the classification proposed by Villermaux [23] in entrained, fluidized and stacked reactors (see Table 1). Falling cloud of particles solar reactors such as the receiver described before–in case it had chemical proposal- should be included among the entrained type reactors. Selecting one type of particles solar reactor may fundamentally depend on the type of application. Villermaux [23] recommended the use of fix beds, included in the stacked reactors group, for solar catalytic reactions. For those reactions that require good thermal transfer properties, he suggested the employment of fluidized beds. The close contact between gas and fluidized particles favours a homogeneous heating at the reaction medium. Moreover, higher temperatures are expected to be achieved. His recommendation about entrained reactors varies depending on the sub-type what they belong to. For example, cyclones are interesting if the further separation between solid and gas is desired. Villermaux also mentioned the interest of rotary kilns due to the wide knowledge and experience existing already on solid treatment in this type of reactors. Some other classification criteria could have been employed to distinguish types of solar reactor. Application is one of the possibilities selected by other authors. For example, Puig-Arnavat et al. [24] published in 2012 a state of the art on solar reactors applied to the

gasification of carbonaceous feedstock or Steinfeld [25] relates different solar reactors to different routes for hydrogen production through thermochemical routes.

Since the initial investigations on the particles solar reactors, many authors have designed different prototypes with their particular characteristics. Villermaux's selecting criteria have not been always followed; nevertheless the compilation that is presented in this work distinguishes between entrained, fluidized and stacked reactors.
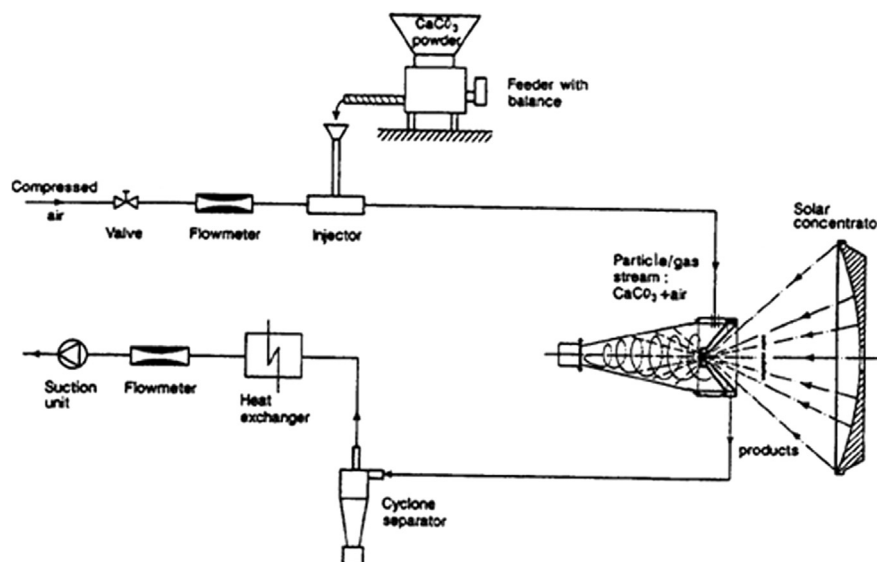
3.1. Entrained reactors

While SNL were starting to develop the first concepts regarding SPCR, chemical engineers from CNRS-ENSIC, France [26], thought out a cyclone as an innovative concept of particle solar reactor. It was purposed to study the continuous flash pyrolysis of wood sawdust at 1143 K. Results concluded that such a reaction could be carried out on a large scale in such a new type of reactor by use of concentrated solar energy.

In 1991, Imhof et al. [27] proposed a new solar cyclonic reactor conceived to develop gas–solid thermochemical processes. With this concept, an easy way to continuously feed reactants and remove products was sought in combination to some of the advantages of volumetric receivers such as high absorbance of radiation [27]. The cyclonic reactor, shown in Fig. 2, consisted of a truncated conical cavity 30 cm-height that was opened to the atmosphere. Inner walls were covered by a ceramic insulation layer. The remainder of the cavity was formed by two concentric cones that formed a conical gap for the gas exhaustion. The reactor was designed to be used at the Paul Scherrer Institute (PSI) 17 kW solar furnace. The authors studied the thermal decomposition of calcium carbonate as an example of gas–solid reaction. Employed experimental set-up, shown in Fig. 2, mainly included a gas and particle injection system, the solar reactor, a cyclone separator for collecting solid products, and a heat exchanger to cool down the outlet gas stream. They reported to have achieved reactants temperatures about 1300 K, high degree of calcination and a global efficiency of 43%. This efficiency is based on the ratio of the overall energy absorbed, sensible and process heat, to the energy incident on the aperture. A further prototype, of same configuration but larger dimensions was fabricated and tested at the 55 kW McDonnel Douglas dish [28].

Table 1
Gas–solid reactors classification proposed by Villermaux in 1980 [23]. Falling particles reactors were not included in the original classification. However it has been added to the Villermaux's table taking into account the previous section of this work.

Stacked beds	Fixed	
	Mobile	Conveyor belt
		Blast-furnace
	Brewed oven	Multistage
		Rotary kiln
Fluidized or suspended beds	Vibrated or pulsated	
	Fluidized bed	
	Circulating fluidized bed	
	Blown bed	
	Drooping bed	
Entrained beds	Pneumatic transport	
	Cyclone	
	Falling particles	

Fig. 2. Scheme of the cyclonic solar reactor and experimental set-up reported by Steinfeld et al. [28].

A novel solar chemical reactor was designed in 1998 by Steinfeld et al. [29] also based on a vortex flow confined to a solar cavity-receiver. A small prototype of 5 kW, called *SynMet* was firstly fabricated and tested at the PSI solar furnace. It was conceived for the co-production of metallic Zn and syngas starting from ZnO and natural gas (NG). It consisted of a cylindrical cavity provided with a quartz window. Concentrated radiation entered through the window and heated the reactants and the cavity walls. Particles of ZnO, conveyed in a flow of NG, were continuously injected into the cavity via a tangential inlet. A vortex flow of reactants progressed from the back to the front of the reactor. Achieved temperatures exceeded 1600 K and chemical conversion from ZnO to Zn reached 90%. An innovative incorporation on this reactor design was the actively cooled window. An auxiliary flow of gas was injected tangentially and radially at the window in order to maintain it cooled and clear of particles. This reactor was further employed to produce CaO and syngas by the combined $CaCO_3$-decomposionand CH_4-reforming processes [30]. SYNPET project (2003–2009) resulted in a solar reactor similar to *SynMet* but applied to the steam-gasification of petcoke. Main modifications were associated to the reactant feeding system that, after several attempts, was finally a slurry generator [31,32]. The reactor tested in a high-flux solar furnace in the range 1300–1800 K yielded up to 87% petcoke conversion. The solar-to-chemical energy conversion efficiency attained 9% without accounting for the products sensible heat, and 20% when the sensible heat was recovered for steam generation and pre-heating. The vortex reactor was then scaling up from 5 kW to 300 kW [33,34]. Scaling up improved the solar-to-chemical efficiency to 24% due to the advantageous volume-to-surface ratio. It was also found a big dependence of the conversion to the particle size and residence time inside the reactor. Fig. 3 shows both schemes of 5 kW reactors, the one proposed in 1998 and the subsequent in 2006.

Researchers at Weizmann Institute worked on a new solar cyclone reactor to perform the thermal splitting of methane. Such a configuration was chosen in order to allow an effective reactor window screening and to keep it free of generated carbon particles. Thus, first efforts were destined to analyze the advantages of a tornado flow in an unseeded reactor provided with a transparent window [35].Temperatures up to 1320 K were achieved and the maximum extent of reaction reported was 28.1%. The main problem found was a high degree of carbon deposition on the reactor walls and also on the exit port, what often triggered the experimental test termination. In order to favor the generation of carbon particles by methane splitting in the central region on the chamber instead of the walls, it was

proposed to seed the reaction chamber with radiation absorbing particles [36]. This way, temperature was increased at the middle of the cavity. However, it was necessary to prevent destruction of the reaction window by contact with incandescent solid particles. Different geometries were examined in order to optimize the reactor design. Fig. 4 shows the last proposed geometry that was considered a satisfactory solution. The main reactor body was composed of three segments. Main gas streams were introduced through a distributor assembled at the top of the reactor to generate a tornado flow pattern inside the chamber. Two extra gas enters were located between the segments and seeding gas can be injected optionally through either one of the lateral ducts d_1, d_2 or d_3.

On the basis of a cloud of particles absorbing solar direct radiation Ganz et al. [37,38] proposed in 1994 a novel reactor concept. It consisted of a cylindrical cavity of heat-resistant steel that contains a windowless aperture. Reactants in powder impinged on a cone and were conveyed in a swirling air stream. They were directly exposed to high solar flux. The radial air jet helped to prevent the particles from leaving the reactor. Products exited via a water-cooled axial tube where reactants were quenched. A schematic of the solar reactor is represented in Fig. 5.

From previously mentioned experiences, it can be inferred that vortex-flow based reactors are normally feasible choice for heating
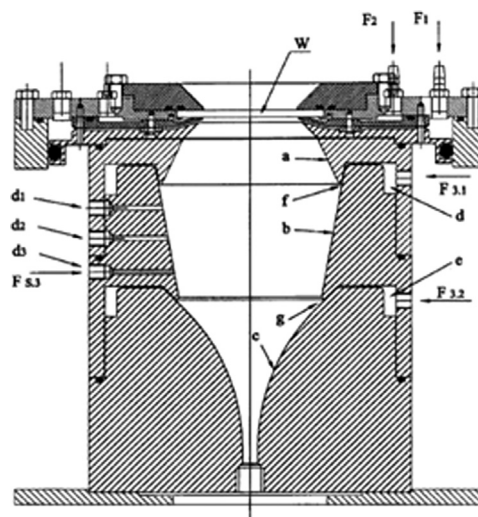

Fig. 4. Satisfactory geometry selected by Kogan et al. to create a proper tornado flow preventing the window destruction [36].
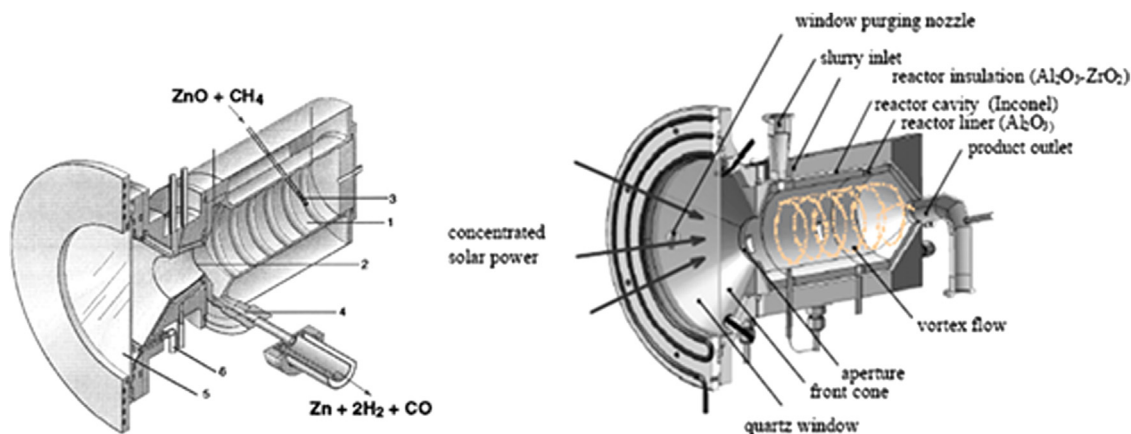

Fig. 3. Schemes of the two 5 kW vortex flow reactors. Left: Prototype designed for ZnO reduction with NG [29]. Right: Prototype designed to the steam-gasification of petcoke [32].
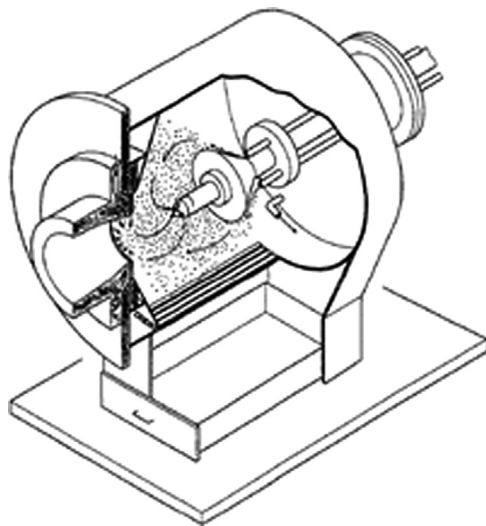
Fig. 5. Solar reactor proposed by Meier et al. [38].

1: Fluidized bed
2: Solar radiation
3: Distributor
4: Bracket
5: Silica tube
6: Gas inlet
7: Gas outlet
8: Thermocouples
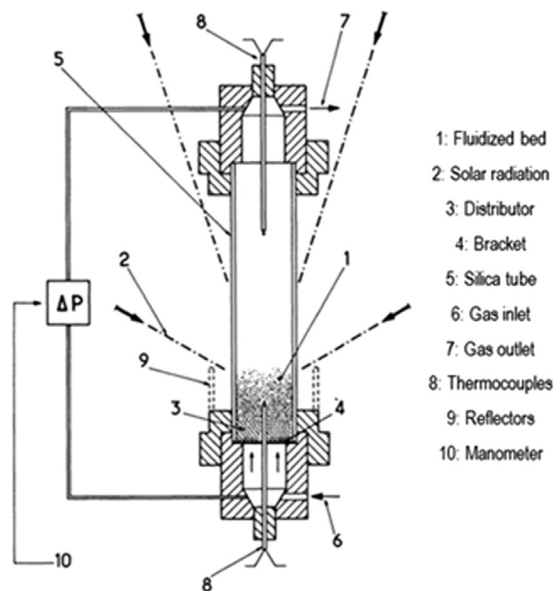9: Reflectors
10: Manometer

Fig. 6. Scheme of the lab-scale fluidized bed proposed by Flamant et al. [40].

solid particles in the range of 1300–1800 K, that are common for many thermochemical reactions (for solar fuels production, thermochemical storage, etc.). Geometry of the cavity and injection of gas and reactants are the main aspects to take into account to get a properly designed prototype.

3.2. Fluidized reactors

In comparison to entrained reactors, fluid beds improve gas–solid contact and increase particles residence time. Such a characteristic may represent an advantage particularly for those chemical reactions associated to slower kinetic mechanism. An early solar fluidized bed was proposed by Flamant in 1980 [39]. It consisted of a transparent silica tube (34 mm in diameter) between two metallic brackets. The tube was directly irradiated by concentrated solar radiation (Fig. 6). This device was tested in a 2 kW solar furnace for heating refractory materials at 600–1300 °C and decarbonation of calcite at 850 °C. Graphite particles were attached with calcite in order to increase the chemical rate. Thermochemical conversion was also improved with graphite upper to 14%. The scaling-up to 50 kW of this reactor was then

realized by Flamant et al. [40]. Other concepts improving this prototype were later proposed [41] such as an opaque fluidized bed provided with a transparent window on the top or an annular fluidized reactor with opaque external walls that is also irradiated from the top.

Preliminary solar and non-solar thermochemical tests are often carried out in a laboratory scale fluidized bed due to their easy construction and operation. Fig. 7 shows a small solar fluidized reactor designed by Steinfeld et al. [42] to perform the ZnO reduction and CH_4 reforming. It consisted of a 2 cm in diameter quartz tube. A compound parabolic concentrator (CPC) and an involute provided uniform irradiation on the tubular reactor. With this arrangement the design offered high thermal efficiency, low thermal capacitance and good thermal shock resistance. ZnO particles were fluidized in CH_4 and reaction was activated by the concentrated radiation given by the PSI solar furnace. The fluidized-bed, operated under vigorous bubbling conditions, was likely to be at uniform temperature. The reactor-receiver operated at 1373 K and under uniform solar flux of 57 W/cm^2 system exhibited very low thermal inertia, good termal shock resistance and proved to be well adapted for direct absorption processes. A maximum of 43% of the CH_4 in the reducing gas was converted.

A similar design, showed in Fig. 8 was employed in 2009 to perform consecutively CaO-carbonation and $CaCO_3$-calcination to
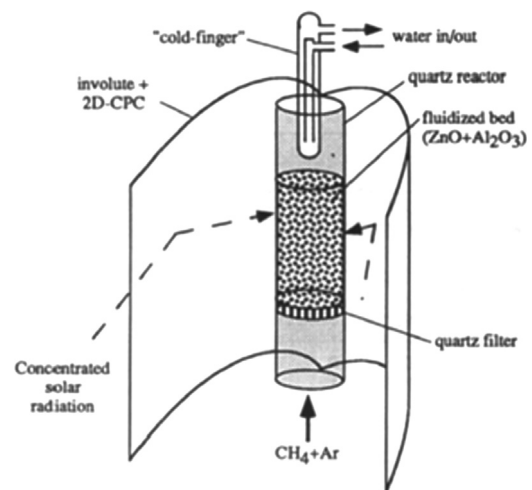

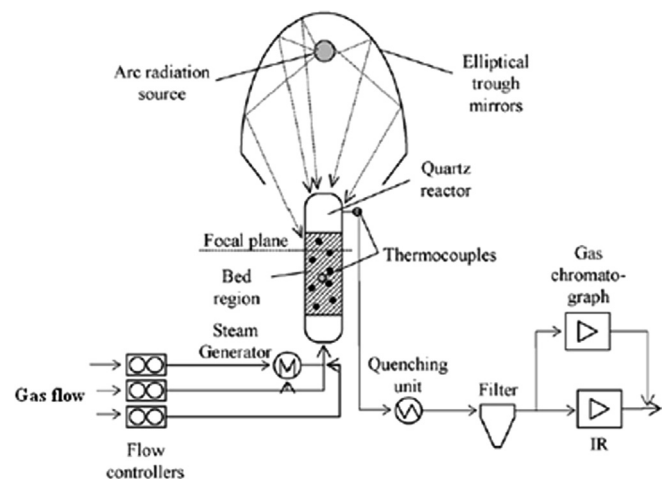Fig. 7. Scheme of the solar fluidized bed proposed by Steinfeld et al. [42].

Fig. 8. Fluidized solar reactor tested in the PSI high flux solar simulator and set up of the process [43].

capture CO_2 from atmosphere [43]. Solar reactor also consisted of a quartz tube, 25 mm-outer diameter, 25 cm-height, containing a fluidized bed of reacting particles. A high flux solar simulator was employed to irradiate the tube at its top with a power up to 75 kW. Simulator focal plan was located at the middle of the fluidized bed. Successful results were obtained with a mass balance of CO_2 after five consecutive cycles close to 99%. Maximum temperatures of 1150 K were achieved for the calcination step.

Gokon et al. [44] proposed a novel solar fluidized bed. It was based on the concept that concentrated solar radiation passed through a transparent window on the top of the reactor and directly heated an internally circulating bed of reactant particles. They specifically used $NiFe_2O_4/m\text{-}ZrO_2$, which two-step thermo-chemical cycle was investigated. On the basis of this concept two laboratory reactors were developed (Fig. 9) and tested using a 6 kW Xe-arc solar simulator. The employed input of power was 2.4–2.6 kW. First one was constructed using quartz tubes, with an outer diameter of 45 mm. Carrier gas was introduced through a conical cap and a draft tube in order to create an internally circulating bed. The reactor was preheated at 900 °C. A second fluidized reactor was constructed of stainless steel with approximately the same dimensions. A quartz window was located at the top of the reactor to let the concentrated radiation enter in the reactor. Chemical conversion was found to increase by including a draft tube in the reactor design that is, generating an internal circulation. Moreover, better results were achieved with the stainless steel prototype, presumable due to an increasing on the thermal efficiency caused by the opaque walls. The stainless steel reactor was later employed to perform both successive reactions of thermal-reduction and water-decomposition steps, also starting with $NiFe_2O_4/m\text{-}ZrO_2$ particles [45]. The gas feed was switched from an inert gas in thermal decomposition to an inert gas and steam mixture in water decomposition. This second reaction was performed under 1.6–1.7 kW of incoming power. Successful hydrogen production was achieved with a reported chemical conversion of 45% and maximum measured temperature of 1200 °C.

Several authors have studied the solar gasification process in a directly irradiated fluidized bed reactor [24]. This is the case of the beam down irradiated fluidized bed concept proposed by Gokon et al., what was applied for the CO_2 gasification of coal coke with successful results. It was reported a maximum energy conversion efficiency of 14%. Some other examples of fluidized bed employed

1 45° Mirror
2 Sample position
3 Hammer
4 Inert gas inlet
5 Tracer inlet
6 Three-way/two-position valve
7 Quartz tube
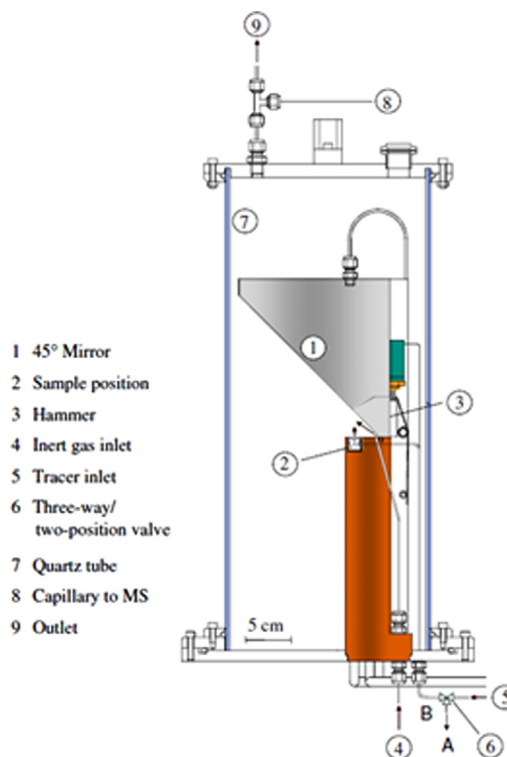8 Capillary to MS
9 Outlet
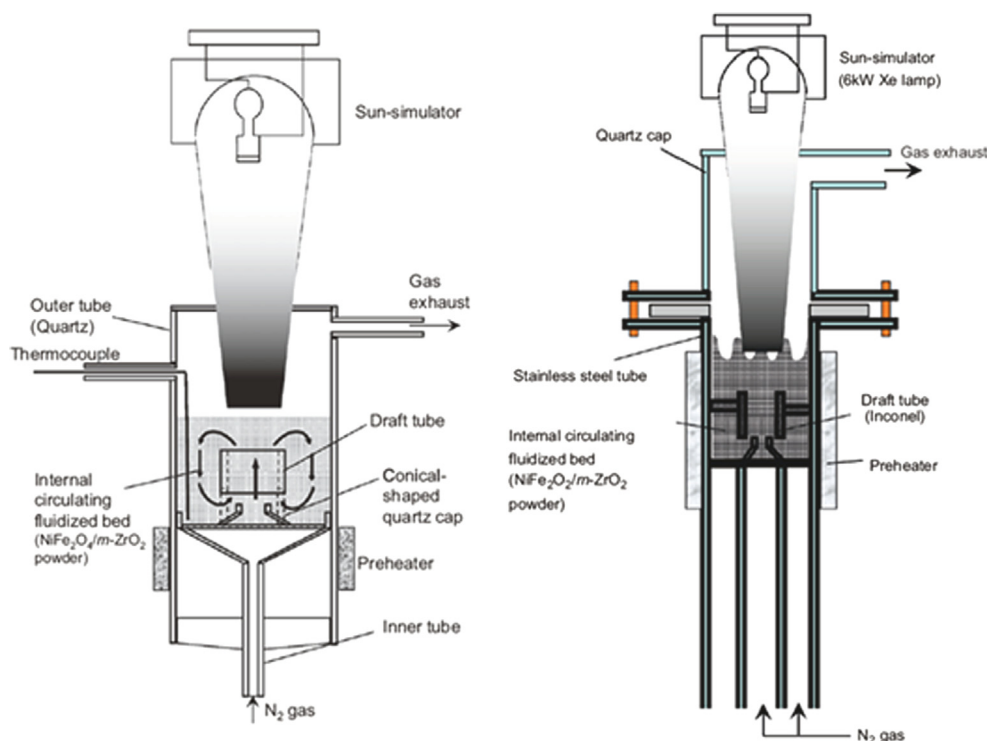
Fig. 10. Side view of TREMPER [47].

Fig. 9. Internally circulating fluidized solar reactors proposed by Gokon et al. Left: quartz prototype. Right: stainless steel prototype [44].

for solar gasification of carbonaceous material are compiled in [24] carried out by centers such as ETH and University of Minnesota.

3.3. Stacked reactors

According to the classification reported by Villermaux [23] it is appropriate to distinguish between fixed, mobile and rotary reactors or kilns. In general terms, it has been observed that rotary reactors favor mass and heat transfer phenomena. However, design, construction and operation on fixed reactors are usually easier and more economic. Particularly, those prototypes conceived as small and preliminary laboratory tools to start studying chemical processes are often simple fixed bed.

3.3.1. Fixed reactors

TREMPER is a fixed reactor developed by Frey et al. [46] to study chemical kinetics of reactions on a second scale at temperatures up to 2100 K. TREMPER was composed of a set of elements all of them enclosed in a quartz tube (Fig. 10). The sample was placed in a shallow hole on a water-cooled copper support. This arrangement prevented the sample from reacting with the support. A 45° mirror guided the concentrated solar radiation from a horizontal source to the sample. Carrier gas swept the quartz tube and was collected with a silica capillary. A gas flow was directed towards the mirror to avoid deposition of evaporated material. A quenching unit was included at the outlet. A flow patterns analysis determined the whole apparatus behaved as a continuous ideally stirred tank [47] and hence, gas release rates could conveniently be obtained from on-line gas analysis at the outlet. Reduction of iron and manganese oxides were performed at TREMPER and maximal chemical conversion reached was 25% for iron oxide and 85% for manganese oxide.

A pattern flow analysis was also done by Alonso et al. to study the behavior of a 1 kW solar reactor conceived to perform thermal reductions of non-volatile metallic oxides [48]. The solar reactor is schematically represented in Fig. 11. It consisted of a vertical stainless steel and internally insulated vessel 100 mm high and 80 mm in diameter that was closed to the ambient by a quartz window. Concentrated radiation provided by a 7 kW_e solar simulator is guided by a 45°-sloped water-cooled mirror towards the cavity of the reactor. Samples were introduced inside a crucible forming a packed-bed of particles. Carrier gas was introduced into the reaction chamber to sweep it and collect gas products. Flow into the reactor was found to behave close to an ideal plug flow.
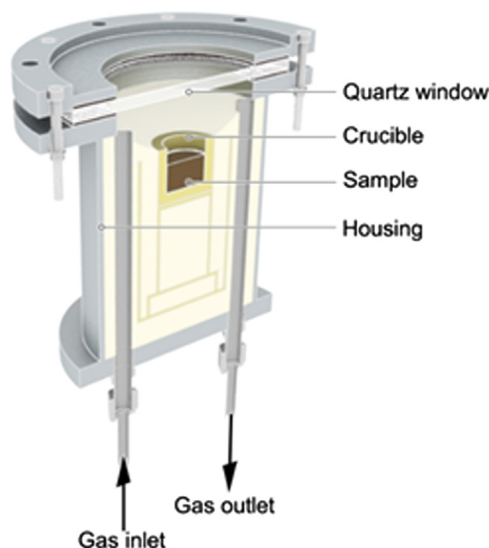

Fig. 12. Schematic section of the reactor developed by Alonso et al. [49].

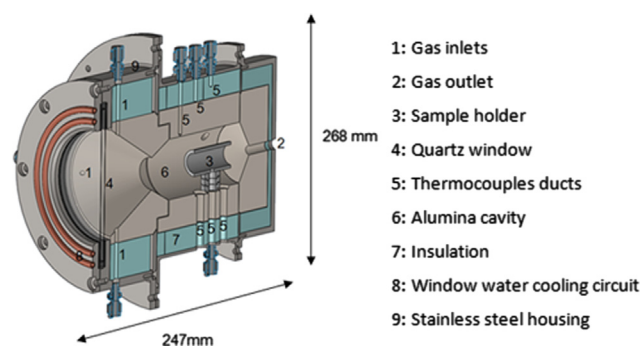1: Gas inlets
2: Gas outlet
3: Sample holder
4: Quartz window
5: Thermocouples ducts
6: Alumina cavity
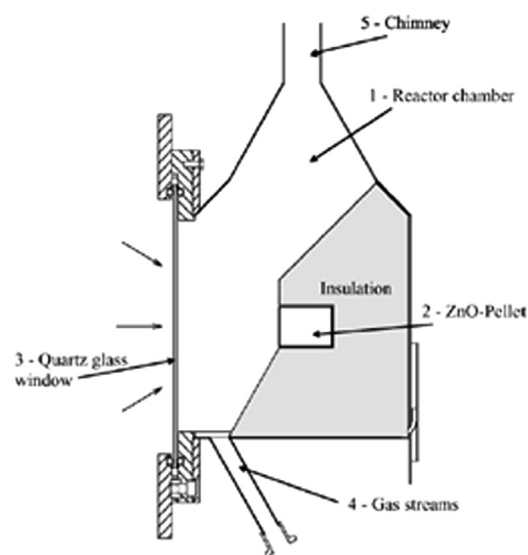7: Insulation
8: Window water cooling circuit
9: Stainless steel housing

Fig. 13. Fixed reactor developed by Moller and Palumbo [50] to dissociate ZnO.

Manganese oxides, Mn_2O_3 y Mn_3O_4, were reduced at the top layer of the packed-bed with a maximum conversion of 60% for Mn_2O_3. A maximum temperature of 1400 °C was measured at the top of sample. However, high thermal gradients were produced between the irradiated surface and the bottom of the sample.

Similar flow pattern characterization as well as thermal tests was done on a novel 2 kW prototype designed by Alonso et al. [49] (Fig. 12). The solar reactor mainly consisted of a central alumina cavity 110 mm length and 60 mm in diameter closed at the front by a cone, also made of alumina and by an alumina cover at the back. There was placed the gas outlet. The cone included a water-cooled quart window. The housing, made of stainless steel was separated from the cavity by an insulation layer. Gas inlet took place by four perforations located in cross at the frontal cone. After crossing the cavity it left through a duct placed at the back of the reactor. Reactants were packed inside a 20 mm inner diameter, 26 mm outer diameter and 50 mm in length cylindrical ceramic sample-holder that rested in the middle of the cavity. Radiation entered through the quartz window and an aperture. It was found that the fluid flow behavior was closed to an ideal Plug Flow Reactor, particularly at high temperature and high carrier gas flow. An effective thermal efficiency of 47% was achieved at 530 W of incoming power. High thermal gradients were found at sample with a maximum measured temperature of 1450 °C. Reductions of Mn_2O_3, Mn_3O_4 and CeO_2 were performed achieving complete conversion for the first one and variable for the rest, depending on the reaction conditions.

Fig. 11. Schematic of the 1 kW vertical solar reactor developed by Alonso et al. [48].

Moller et al. [50,51] also employed a fixed reactor to dissociate pre-sintered ZnO. A schematic of the reactor used is shown in Fig. 13. The reactor chamber was filled with stabilised ZrO_2 insulation. In the center of the chamber, at the focal point of the solar furnace, a ZrO_2 receptacle accepted a cylindrical pellet of ZnO. Concentrated solar energy passed through the window and illuminated the ZnO front surface. Several inert gas streams prevented products vapor from condensing on the window. The gaseous reaction products and the inert gas flowed continuously through the reactor to a chimney and out to a heat exchanger where the products were quenched. Temperatures up to 2100 K were achieved at the sample.

To study the reduction step of the CeO_2 based water splitting thermochemical cycle, Abanades et al. [52] developed a solar device consisting in a spherical vessel of Pyrex ™ which permitted a pellet of reactant heating by concentrated solar energy and the control of atmosphere composition and pressure. It is shown in Fig. 14. This kind of solar reactor was closed to air and it could operate under controlled atmospheres: vacuum, inert or reactive gases. Results showed that total thermal reduction of Ce (IV) to Ce (III) could be obtained working with proper parameters such as initial sample mass, reaction time, pressure and sample temperature. Successful results also depended on the gas flow hydrodynamics surrounding the sample. Temperatures of 2000 °C were detected at the sample because it was observed CeO_2 melting. A post-treatment characterization of the sample revealed high thermal gradients in the sample.

Chueh et al. [53] studied the solar thermochemical H_2O–CO_2 splitting cycle using also cerium oxides. A novel fixed solar reactor was employed to perform the two stages that are involved in such a cycle, first one at higher temperature and second at lower temperature. A schematic of the solar device was shown in Fig. 15. It consisted on a thermally insulated cavity receiver containing a porous monolithic ceria cylinder. Concentrated solar radiation entered through a windowed aperture and impinged on ceria

inner walls. Reacting gases flowed radially across the porous ceria toward the cavity inside, whereas product gases exited the cavity through an axial outlet port at the bottom. The feasibility of the complete cycle was demonstrated and stable and rapid generation of CO and H_2 was achieved by dissociating CO_2 and H_2O. Material stability was also demonstrated over 500 thermochemical cycles. However, solar-to-fuel efficiencies of 0.7–0.8% were only achieved. Authors suggest thermal transfer controls the high temperature stage of the process. Moreover, low efficiency was also attributed
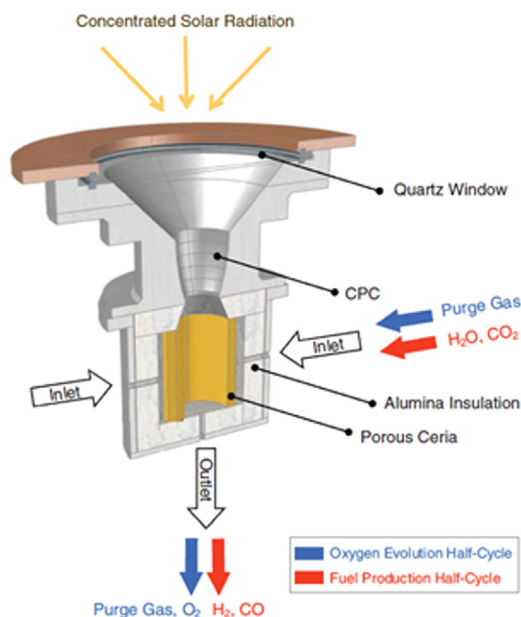

Fig. 15. Schematic of the solar reactor proposed to study the solar thermochemical H_2O–CO_2 splitting cycle [53].
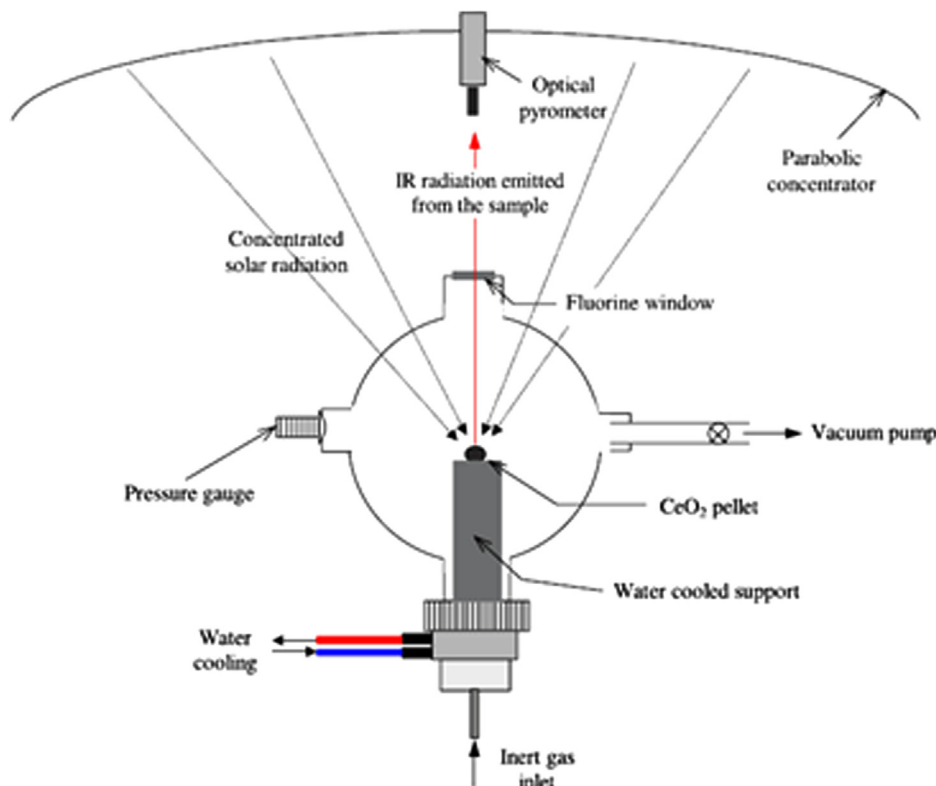

Fig. 14. Solar reactor used by Abanades and Flamant [52] to reduce CeO_2 under controlled atmosphere.

to the system scale and design, due to it is limited by thermal losses. Thus, the need of a reactor optimization was suggested.

As a part of the two-step thermochemical water splitting cycle the high-temperature thermal reaction of ZnO and SnO_2 was also investigated by Chambon et al. [54] in a 1 kW solar fixed reactor. It was composed of a cylindrical water-cooled shell (depth: 76 mm, diameter: 88 mm) made of stainless steel. It was close to the ambient by a convex window made of Pyrex ™. The cavity was internally coated with a ceramic insulation. Pellets of reactant were stacked in a ceramic tube exceeding of 7 mm the bottom of the refractory cavity. They formed a rod that was pushed upward via a screw piston manually rotated for achieving a continuous reactant injection during an experimental run. Temperatures of 1900 K were measured at the cavity. Kinetic parameters for ZnO and SnO_2 dissociations were obtained. Although the yield of product particles recovery was not very high (around 2%), authors expected to achieve better results by optimizing a quenching device at the reactor output. Fig. 16 shows and scheme of this reactor.

A different concept of solar fixed reactor led to a novel design developed by the Tokyo Institute of Technology, (Japan). It was conceived for solar hydrogen production with two step water splitting process. The basis of the reactor were two fixed cells located onto a rotor that switch two different type reaction rooms, one for discharging oxygen and another for water splitting reaction. The reactor rotated in order to alternate the reaction cell that is exposed to concentrated solar radiation. Fig. 17. Shows a schematic outline of the rotary-type solar furnace for two-step water splitting cycles. Experiment performing two thermochemical cycles, CeO_2 and Ni,Mn-ferrite, were developed in a laboratory scale reactor and using an infrared lamp as heat source [55]. Repetition of the two stages of both process were achieved, and successive evolution of H_2 and O_2 in respective water splitting and reduction cell were observed. Optimum reaction temperatures found were 1623 K and 1273 K in case of CeO_2 cycle and 1473 K and 1173 K for ferrite cycle. The solar reactor was scheduled to be scaled-up and operated at the solar concentrating system of CSIRO, using an input solar power of 10–30 kW. This work was developed in the frame of the Asia-Pacific Partnership on Clean Development and Climate project [56].

The idea of rotating reaction cells also led to develop another concept in SNL. The main objective was to perform ferrites thermochemical cycles [57]. It was called Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5) and used a stack of counter-rotating rings or disks with fins along the perimeter. The fins contained ferrite reactant, presumably on a support. Each ring rotated in the opposite direction to its neighbor at a rotational speed on the order of one RPM or less. Solar flux illuminated the fins on the stack of rings on edge along nominally 1/4 of the perimeter. On the opposite side of the stack, the water oxidation reaction took place. The remaining half of the stack (two 1/4 sections between) was adiabatic and is utilized for counter current recuperation occurs, primarily by thermal radiation. Equal pressures are maintained in the two reactors to minimize flow through the recuperator sections. Fig. 18 shows a schematic of the CR5, with a detail of the set of counter-rotating rings. Preliminary thermal efficiency reported was 29.9% although it depended on operating temperature and the irreversibility of their internal
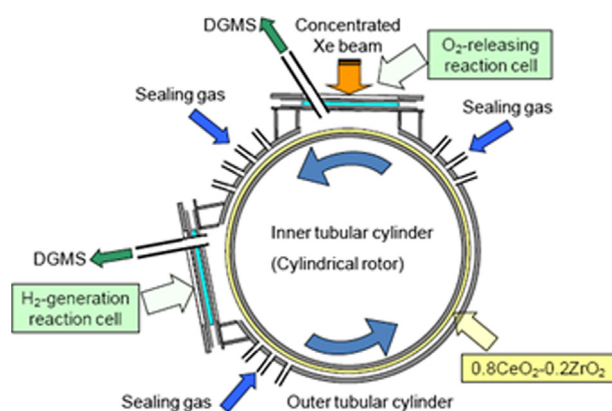

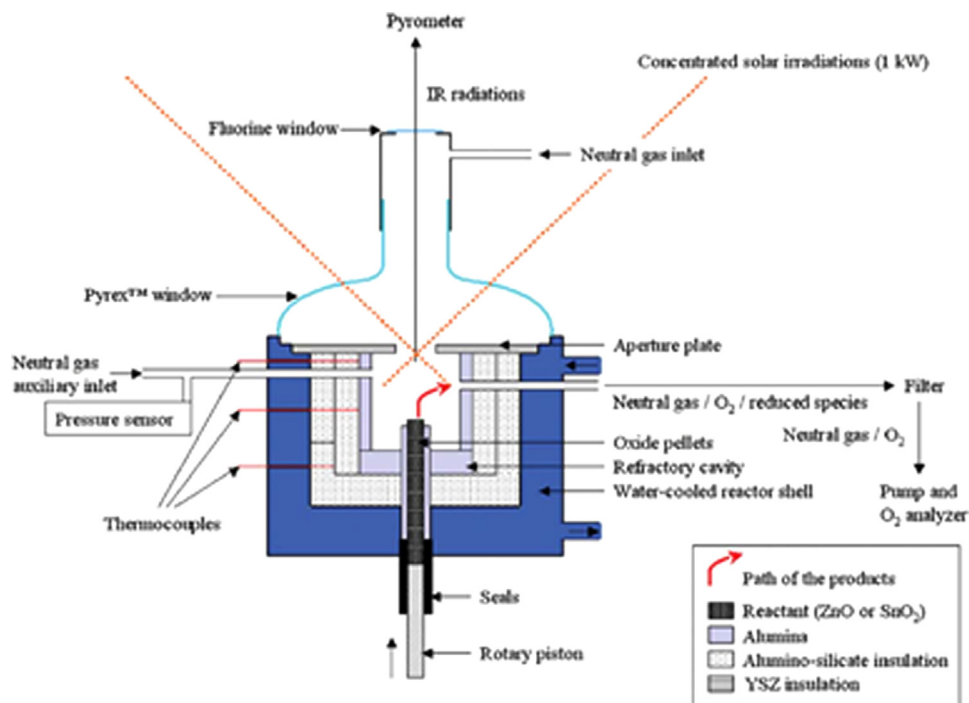Fig. 17. Novel solar reactor developed by the Tokyo Institute of Technology [55].

Fig. 16. Fixed solar reactor developed by Chambon et al. [54] to investigate the high-temperature thermal reaction of ZnO and SnO_2.
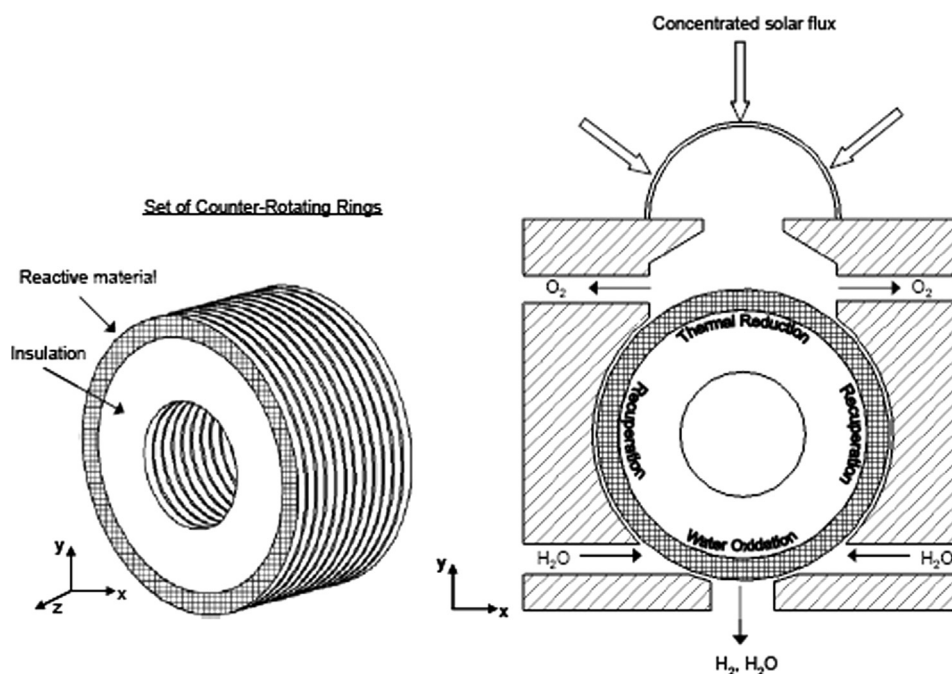
Fig. 18. CR5 reactor. Left: Detail of the set of counter-rotating rings. Right: General scheme of the solar reactor [57].
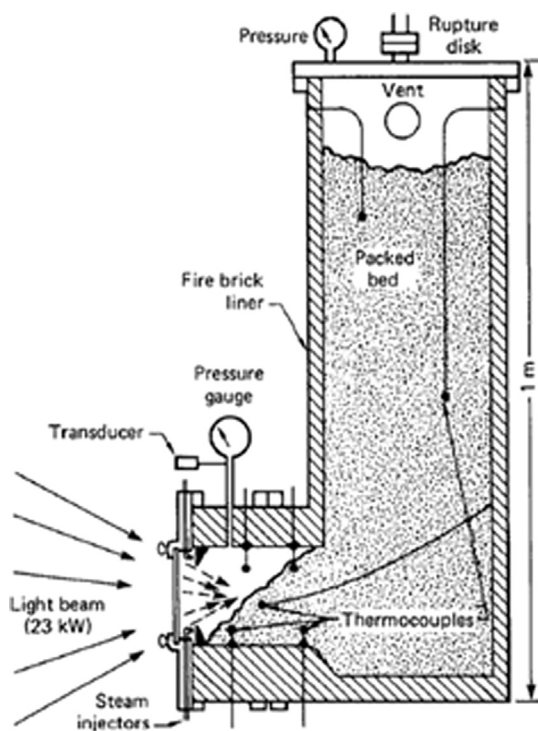

Fig. 19. Packed-bed type gasifier designed by Gregg et al. [58].

processes. The maximum temperature reported at the reduction step of FeO was 2300 K.

This section should also consider a packed-bed gasifier proposed by Gregg et al. [58] for the gasification of carbonaceous material. It is shown in Fig. 19.

The reactor was constructed with a stainless steel pipe (with 30 cm internal diameter) and it has a L-shape. This way the fed is done only by employing gravity. Walls are insulated with a firebrick liner. On the short side of the L, it is placed a silica window with an aperture through what the sunlight enters. Steam

or CO_2 was introduced through the inlets placed around the perimeter of the window and the outlet was placed on the top wall of the reactor. Gasification of coal, activated carbon, coke and a mixture of coal and biomass were carried out in this reactor with a maximum solar power input of 23 kW. The gas production rate of CO_2 gasification increased with increased solar power, and when steam was used for gasification, the gas composition and heating value were almost independent of solar power. It was found a considerable range of scatter of the energy conversion efficiencies from 19% to 48% for different solar powers.

Based on the same concept, Taylor et al. [59] presented a smaller windowed packed-bed type solar gasifier that was proved in a 2 kW solar furnace. Carbonaceous material was feeding into an insulated central body and steam was spraying on the reactant while it was heated by solar radiation. Energy conversion efficiency of 30% was reached for carbon gasification with steam and 40% for charcoal gasification with CO_2. However efficiency of only 10% was obtained for charcoal gasification with CO_2 by using a fluidized bed reactor.

Examples compiled in this section indicate a common trend to design fix reactors as first small prototypes to start an investigation. Apart of the simplicity of these reactors, they allow measuring reactions parameters, such as reaction temperature, or evaluating the interaction between reactants and radiation. It is also possible to develop parametric analysis and kinetic studies if the reactor design and the process line were it is integrated are appropriate (proper flowpath, gas concentration measuring, etc). However, high thermal gradients are frequently present in the packed-bed type samples. While very high temperatures can be achieved on the surfaces that see directly the radiation, other areas of the sample do not reach reaction temperature due to thermal transfer limitations. That impairs chemical conversion and global efficiency of the process.

3.3.2. Mobile reactors

A representative example of mobile reactors is the one designed by Koepf et al. [60,61] in 2012, abbreviated as GRAFSTRR. It was designed, constructed and tested for the reduction of

Zn power. It was proposed to ensure the reactants were dispersed uniformly in the cavity as like occurring in rotary reactors, without the engineering difficulties associated to them. The reactor is closed to the atmosphere with a quartz window, and features an
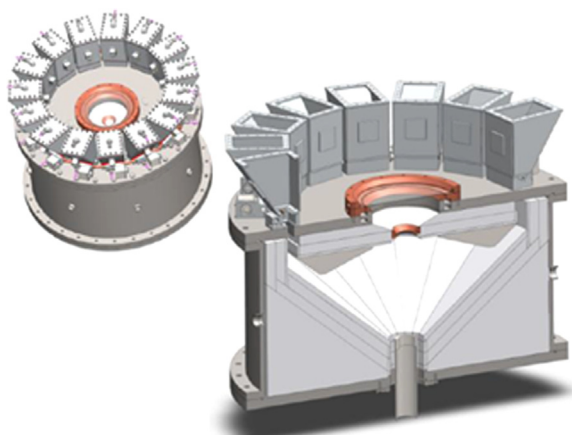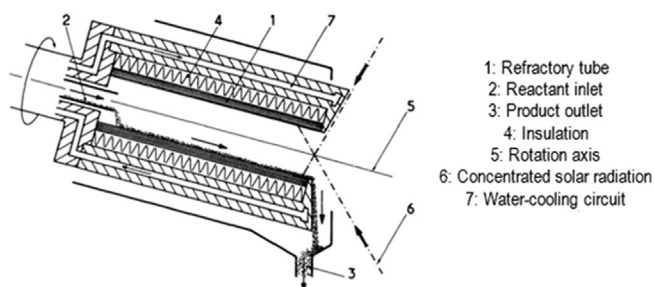
inverted conical-shaped reaction surface along which reactant powder descends continuously as a moving bed, undergoing a thermochemical reaction at high temperature upon exposure to highly concentrated sunlight within the reaction cavity. The cavity inner wall is the reaction decomposition reaction surface is comprised of fifteen trapezoidal pure alumina tiles supported by three layers of porous ceramic insulation, shaped into an inverse cone with a 40° inclination. ZnO powder is fed individually to each tile-surface and it is induced with vibration forming a moving-bed reactive layer. After the dissociation reaction, Zn product vapor is channeled downward into a centrally-located exit because a vortex flow is originated above the aperture plane and connects through the reaction chamber to the exit tube. The reactor, that is expected to operate in the 10–20 kW range, is depicted in Fig. 20. Initial experiments using a high-flux solar simulator successfully demonstrated the mechanical stability of the reactor and primary systems, namely particle entrainment in the vortex flow, moving bed adhesion to the reaction surface, and the solid particle delivery and exit mechanism. Temperatures between 1100 and 1900 K were detected on the reaction surface.

Fig. 20. GRAFSTRR reactor and cross-section.

1: Refractory tube
2: Reactant inlet
3: Product outlet
4: Insulation
5: Rotation axis
6: Concentrated solar radiation
7: Water-cooling circuit

Fig. 21. Representation of the rotary kiln designed by Flamant et al. [40].

3.3.3. Rotary reactors

Rotary kilns have been widely employed in many industry processes such as calcination of solids, cement and plaster production, food industry, etc. Heat and mass phenomena occurring in a rotary kiln lead to high chemical conversion. Additional advantages are versatility, long life of components and low cost of maintenance [62]. However, an important drawback is the high amount of energy demanded by this type of reactors, originally supplied by fossil fuels. Such a drawback can be eliminated if concentrated solar energy is used as heating source. That entails the integration of the solar radiation with the endothermic process occurring into the reactor. Moncada et al. [63] proposed a theoretical model studying radiative in solar and infrared spectrums, conductive and convective heat transfer. By means of this study, they could determine the optimal values of design
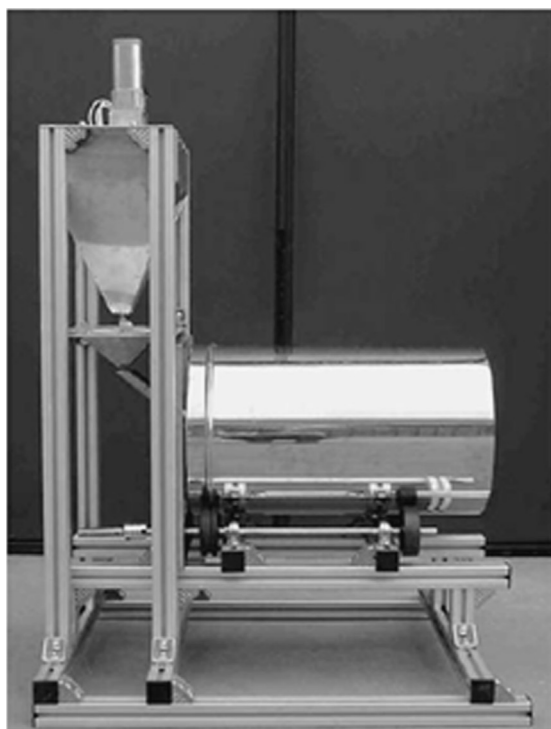

Fig. 22. Pictures of the rotary kiln for producing lime by calcination of calcite [64].

parameters such as carrier gas mass flow rate, concentrated solar energy, inclination angle and rotational velocity. Results were compared to those experimentally obtained with a rotary kiln solar-feed design by Flamant et al. [40]. Difference between experimental and theoretical results did not exceed the 10% for temperature profiles and 5% for output temperature. The rotary solar reactor developed by Flamant et al. [40] consisted of a 5° sloped cylinder (20 mm inner diameter and 90 mm length) composed by a refractory layer, an insulation and a water-cooled housing. It rotated with a constant velocity on which the residence time of reactive particles depended. Thermal gradients of 100 °C/cm took place along the tube. Flamant performed the calcite decomposition and results were compared to those obtained with the fluidized bed cited before. The rotary reactor resulted in a thermochemical efficiency of 30% and maximum temperature of 1500 °C. Flamant's rotary reactor is represented in Fig. 21.

Based on the classical rotary kiln performance, two solar prototypes have been found in literature. In 2004, scientists of PSI, ETH, Valparaíso University and the Italian company QualiCal Srl developed a 10 kW rotary reactor to produce lime by means of the calcination of calcite [64]. It was basically a rotary kiln of 600 mm length and 350 mm diameter that is operated in a horizontal position, as shown in Fig. 22. It had a conical reaction chamber with a fixed cone angle of 5°. The reactants were transported within the conical reaction chamber from the pre-heating zone in the back (feeding side) to the high-temperature zone in the front (discharging side), where the concentrated solar

radiation entered through an aperture placed in the middle of a water-cooled aluminum front shield. The refractory and insulating material was contained in a cylindrical drum made of stainless steel. The reactor worked in a continuous mode. The raw material was stored in a hopper that was placed on top of the rear part of the reactor. A rudimentary discharging system below the front plate collected the end product in bins open to the air. Four rubber wheels driven by a small electric motor generated the rotating movement. During the initial solar experimental campaign, the solar lime reactor operated reliably for more than 100 h during a total of 24 sunny days. The degree of calcination exceeded 98% achieved with temperatures of about 1423 K. However, some mechanical problems mainly associated to the internal refractory material resistance were reported. The solar to chemical efficiency reached 20%. However, authors suggested an optimization of the reactor in order to increase its efficiency.

Another rotary reactor was developed by Neises et al. [65] for thermal reduction and oxidation of cobalt oxide in the framework of solar thermochemical energy storage. The solar rotary kiln consisted of a siliconized silicon carbide cavity, isolated by ceramic fiber plates. The solar radiation entered through an aperture closed by a quartz window. A secondary concentrator is mounted in front of the rotary kiln to direct the incoming solar irradiation into the cavity. The entire equipment is enclosed in an insulated housing and the whole reactor is rotated on wheels driven by a motor. For preliminary test, the redox material was reduced on-sun at temperatures of about 900 °C and re-oxidized off-sun in the same rotary kiln. Experiments were carried out in batch mode. Maximum chemical conversion observed for reduction was 70%. Thirty cycles were performed and no evident degradation was observed. Only half of the material in the reactor was reduced. Authors suggested improvements destined to increase the particles mixing, avoid the particles loss with the gas stream, measure temperatures more accurately and analyze the behavior of the particles during night period. Fig. 23 shows a picture of the rotary kiln in the solar furnace of DLR (22 kW).

A different kind of solar rotary reactor of 10 kW was developed by Haueter et al. in 1999 to perform the thermal reduction of ZnO to Zn and O_2 [66]. Fig. 24 shows a scheme of the prototype called ROCA. It was looked for a reactor concept that respected the chemistry of the reaction and used materials of low thermal capacitance withstanding thermal shocks. The main component was a rotating conical cavity-receiver made of Inconel steel that contained a small aperture to let concentrated solar radiation entered through a window. The window was water-cooled and integrated in a concentric conical shell. The reactants, ZnO particles, were continuously fed axially into the rotating cavity
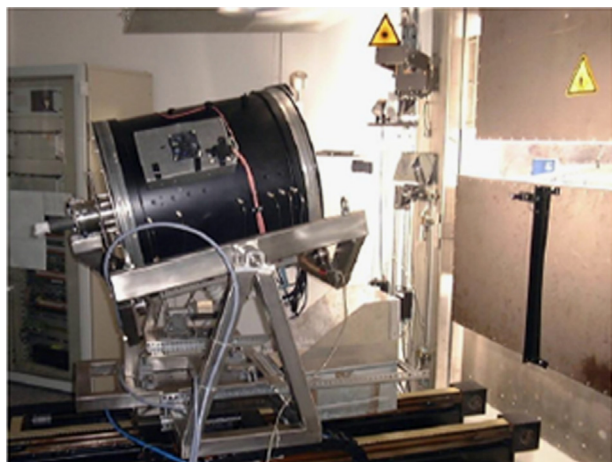

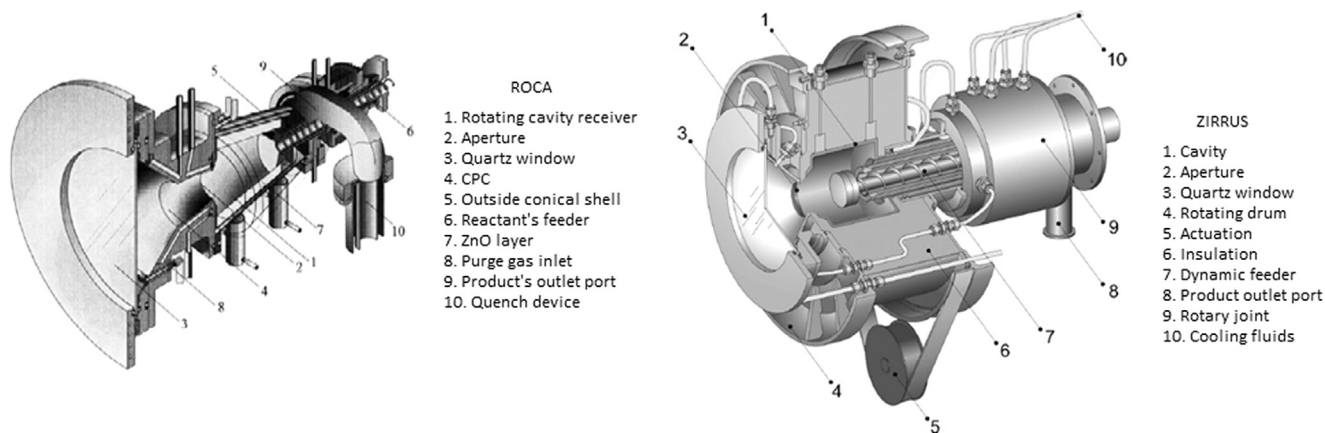**Fig. 23.** Picture of the rotary kiln in the solar furnace of DLR [65].

Fig. 24. Rotary reactors designed to reduce ZnO in PSI. Top: ROCA reactor. Bottom: ZIRRUS reactor [66,67].

with a screw powder feeder located at the rear of the reactor. The centripetal acceleration forced the ZnO powder to the wall forming a thick layer of ZnO that insulated and reduced the thermal load on the cavity inner walls. The gaseous products were swept

out by a continuous flow of inert gas that entered the cavity-receiver tangentially at the front, and exited via an outlet port to a quench device. The purge also kept the window cool and clear of particles or condensable gases. With this arrangement, the ZnO
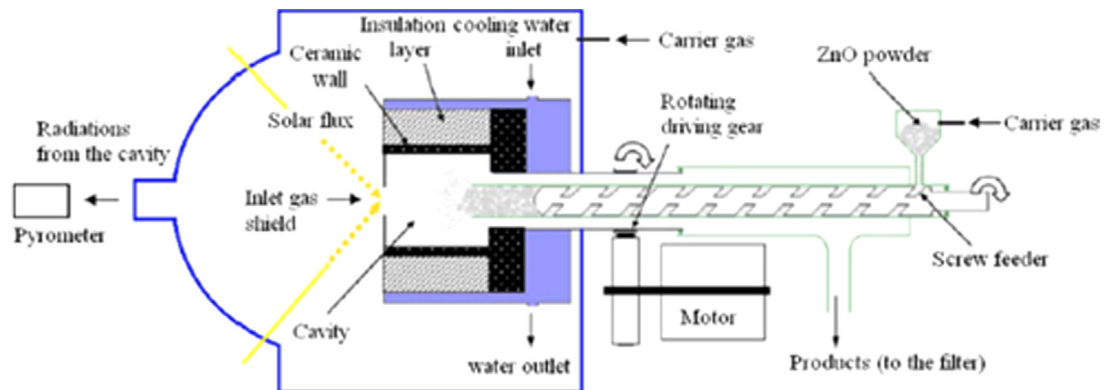

Fig. 25. Rotating cylindrical reactor designed by Abanades et al. [71].

Table 2
Summary of the major characteristics of the most significant reactors considered in the present work.

Author	Solar reactor name	Type	Chemical reaction	Tested in	Power range (kW)	Max. measured temperature (K)	Max. global efficiency (%) (solar to chemical)	Max. chemical efficiency (%)
[27]	–	Cyclonic	Calcite decomposition	PSI solar furnace	–	1300	43	–
[28,29,42,43]	SynMet	Cyclonic	Production of Zn and syngas from ZnO and CH_4	PSI solar furnace	5	1600	–	90
[28,29,42,43]	SynPet5	Cyclonic	Steam gasification of petcoke	PSI solar furnace	5	1800	–	87
[36]	–	Cyclonic	Thermal splitting of methane	Weizmann Institute solar furnace	–	1320	–	28.1
[40]	–	Fluidized	Calcite decomposition	Small solar furnaces Odeillo	2	1573	14	–
[28,29,42,43]	–	Fluidized	Production of Zn and syngas from ZnO and CH_4	PSI solar furnace	–	1373	–	43
[28,29,42,43]	–	Fluidized	CaO carbonation/$CaCO_3$ calcination to capture atmospheric CO_2	PSI solar simulator	–	1150	–	–
[7,44,45]	–	Fluidized	$NiFe_2O_2$/M-ZrO_2 WS thermochemical cycle/ gasification	Niigata University solar simulator	2	1473	–	45
[46,47]	TREMPER	Fixed	MnO_2, Fe_2O_3 and Fe_3O_4 reduction	PSI solar furnace	–	2080	–	80
[48,49]	–	Fixed	Mn_3O_4 reduction	IMDEA Energy solar simulator	1	1673	–	60
[48,49]	–	Fixed	Mn_2O_3, Mn_3O_4 and CeO_2 reduction	IMDEA Energy solar simulator	2	1723	47	100
[50]	–	Fixed	ZnO reduction	PSI solar furnace	–	2100	–	–
[52,54,71]	–	Fixed	CeO_2 reduction	CNRS-PROMES solar furnace	2	2373	–	–
[53]	–	Fixed	CeO_2 based H_2O–CO_2 thermochemical cycle	PSI solar simulator	2	1913	–	2
[52,54,71]	–	Fixed	ZnO and SnO_2 reduction	CNRS-PROMES solar furnace	1	1900	–	2
[55,56]	–	Fixed	CeO_2 and ferrites reduction	Solar Simulator of Tokyo Institute of Technology	–	1623	–	–
[57]	CR5	Fixed	Ferrites thermochemical cycle	SNL solar furnace	9	1697	20	–
[58]	–	Fixed	Gasification of carbonaceous material	The White Sands Solar Facility at the US Army	10	–	–	19–48
[60,61]	GRAFSTRR	Mobile	ZnO reduction	PSI high-flux solar simulator	10	1900	–	–
[39]	–	Rotary	Calcite decomposition	Small solar furnaces Odeillo	2	1773	30	–
[38,64]	–	Rotary	Decomposition of limestone for lime production	PSI solar furnace	10	1423	20	–
[65]	–	Rotary	Thermochemical storage of energy based on cobalt oxides	DLR solar furnace	–	1173	–	70 (reduction)
[66]	ROCA	Rotary	ZnO reduction	PSI solar furnace	10	2000	–	35
[67]	ZIRRUS	Rotary	ZnO reduction	PSI solar furnace	10	1900	–	90
[52,54,71]	–	Rotary	ZnO reduction	2		1273	–	87

served simultaneously as radiant absorber, thermal insulator and chemical reactant. Experimental test concluded the reactor was capable of operating at temperatures near 2000 K with and uniform distribution along the cavity. It also presented a low thermal inertia and high resistance to thermal shock. However some drawbacks were also detected in ROCA design and operation that tried to be corrected with the proposal of a novel reactor of equivalent power called ZIRRUS [67,68]. It was also a rotating cavity in which centripetal acceleration forces the reactant ZnO to cover the cavity. Unlike ROCA, where the ZnO was both the reactant and the insulating material, ZIRRUS decoupled these two functions. Thus ZIRRUS was composed of an inner cavity wall impervious to gas diffusion, but capable of functioning at the decomposition temperature of ZnO in a corrosive environment containing ZnO, gaseous Zn, and O_2. A layer of ZnO of a desired thickness was spread over this surface, with a feeder that extends into and contracts out of the cavity. Packed behind the cavity was principally high temperature resistant insulation. An inert gas was swept across the reactor window and carries the products to the quench device. However, in ZIRRUS the inert gas was preheated above Zn condensation temperature before it enters the cavity. The oxygen diffusion through the walls occurred in ROCA was avoided by using a gas-tight cavity of HfO_2. The product gases flowed between the cold feeder and a water-cooled rotating cylinder wall. The cold wall and the injection of cold Ar promote the quench of Zn to Zn. Tests realized at PSI solar furnace led to successful results. ZnO to Zn conversion exceed to 90%, in comparison to 35% obtained with ROCA. Cavity temperatures of 1900 K were measured. More than 80% of the products were recovered after each experiment, what is an improvement over the 20% recovered from ROCA [66]. A successful reduction of ZnO was demonstrated in further experimental campaigns. Moreover, the reactor was scaled up to 100 kW and it was tested at the 1-MW Solar Furnace in Odeillo [69]. For the large scale prototype, mechanical and thermal resistance were demonstrated [70,71]. ZIRRUS is represented in Fig. 24.

To reduce metallic oxides, Abanades et al. [71] designed a rotating cylindrical reactor (Fig. 25). The cell receiving the solar radiation and the material to be reduced is a water-cooled rotating cavity of 30 mm in diameter provided with an aperture and a hemispherical glass window surrounding. The cell is filled with a ceramic cylinder (e.g. zirconia) surrounded by an insulation layer. The insulated cavity is first heated until thermal steady state. Then, the reactant particles are fed continuously into the cavity with a screw feeder located at the rear of the reactor along the horizontal axis. The solid particles are heated mainly by IR radiation from the hot cavity walls and by direct solar radiation entering the aperture. Studies on the quality of the materials were done as well as ZnO reduction tests. Zinc was significantly produced and recovered with a high purity, and the reactor showed a satisfactory thermal response to concentrated solar flux showed a satisfactory thermal response to concentrated solar flux. The dissociation yield reported is 87% [72]. Temperature reached by the cavity was 1500 °C and above.

4. Conclusions

Since early 80's solid particles have been demonstrate to constitute a proper medium to efficiently absorb radiation. After first studies on particles receiver concepts, gas–solid solar reactors, where particles of reactants directly absorb the radiation have been developed by the main solar chemistry research groups. In this work, an overview of more than 20 particles solar reactors experimentally investigated is offered. Although they have been classified from the classical point of view of gas–solid chemical reactors, no general conclusions on each type of reactor have been identified. Efficiency, maximum temperature

achieved and mechanical or operational problems depend in each case on the quality of design and the radiation power or flux employed for testing. Creating an optimized solar reactor often requires several previous attempts. Complex prototypes are being designed currently with the support of the knowledge previously acquired. In many cases modern solar reactors are the results of correcting design or operational problems detected in older similar prototypes. Most detected problems are associated to material resistance and small chemical conversion due to an insufficient radiation power or a bad use of it (and thus, required temperature is not achieved). Acquired experience is also valuable for scaling up. This way, it is recommended to solve as much as drawbacks as possible in small scale reactors in order to avoid them when a larger, less manageable and more expensive prototype is fabricated. A summary of the main characteristics of the most the reactors compiled in this work is presented in Table 2. Empty cells are due to the non-existence of the parameter or the authors do not provide the corresponding information. Global efficiency is defined as the ratio of process heat used for the chemical reaction to the solar power input. Note that chemical efficiency reported in every case strongly depends on the process duration. This way, if the residence time of reactants inside the reaction chamber is higher, a higher yield should be obtained.

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